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R & T Code 3132111

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Technical Report No. 8

Excited-State Complexes of Conjugated Polymers.

by

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Published

in

Advanced Materials

University of Rochester
Department of Chemical Engineering
Rochester, NY

March 20, 1995

19950403 018

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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 20, 1995	3. REPORT TYPE AND DATES COVERED Technical Report # 8	
4. TITLE AND SUBTITLE Excited-State complexes of Conjugated Polymers			5. FUNDING NUMBERS N00014-94-1-0540	
6. AUTHOR(S) S. A. Jenekhe			Kenneth J. Wynne R & T Code: 3132111	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemical Engineering University of Rochester 206 Gavett Hall Rochester, NY 14627-0166			8. PERFORMING ORGANIZATION REPORT NUMBER # 8	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER DTIC SELECTED APR 04 1994 F	
11. SUPPLEMENTARY NOTES Published in <i>Advanced Materials</i> , Vol. 7, No. 3, 1995.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Recent research on the role of supramolecular structure and morphology on the photophysics of conjugated polymers has resulted in the discovery of their excited-state complexes. Intermolecular excimers are found to play a central role in the photophysics of conjugated polymers. Exciplexes of conjugated polymers are suggested to hold potential for more efficient optoelectronic devices through the ready regulation of luminescence, charge transport, and charge photogeneration.				
14. SUBJECT TERMS Excited-State complexes; conjugated polymers; exciplexes; excimers; photophysics of polymers; electronic polymers.			15. NUMBER OF PAGES 10	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

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Excited-State Complexes of Conjugated Polymers

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1. Introduction

Electronically conducting polymers^[1-3], which have been of wide interest as advanced materials for diverse technological applications, are *ground-state* charge transfer complexes of π -conjugated polymers. In preparing such charge transfer (CT) complexes, the conjugated polymer functions as either an electron donor or acceptor and thus becomes a cation or anion in the CT complex. The counterion in a conducting polymer, often called a dopant, can be an inorganic species, an organic small molecule, or even a polymer^[1,2]. Numerous conducting polymers have been prepared by chemical or electrochemical charge transfer complexation, a process commonly referred to as *doping*, in which the necessary *electron transfer* takes place and the counterion (dopant) is incorporated into the CT complex. The critical and often limiting role of energetics, i.e. the relative energy levels of the donor's highest occupied molecular orbital (HOMO) and the acceptor's lowest unoccupied molecular orbital (LUMO) as measured by the donor's ionization potential (IP) and acceptor's electron affinity (EA), in the ground-state CT process for preparing conducting polymers has long been recognized^[1c]. The realization that the needed free energy for driving charge transfer reactions can be provided by absorbed light has led to the recent discovery of *excited-state* charge transfer complexes (*exciplexes*) of conjugated polymers^[4-6]. Since in principle there are no energetic limitations inherent to donor/acceptor pairs that can form exciplexes of conjugated polymers, their scope may be vastly larger than conducting polymers. Exciplexes of conjugated polymers therefore represent a whole new area of research and development in conjugated polymers and molecular materials, with potential applications ranging from xerographic photoconductors, solar energy conversion, and nonlinear optics to light-emitting diodes.

The fabrication of light-emitting diodes based on injection electroluminescence from poly(p-phenylene vinylene) (PPV) and other conjugated polymers^[7] has catalyzed and accelerated interest in the photophysics of the materials^[4-11]. A central focus of this effort is aimed at the fundamental understanding of the *excited states* and *emission characteristics* of conjugated polymers which are currently not well understood. Although many models have been proposed to rationalize the photophysics of π -conjugated polymers^[8-10], many puzzling features of the solid state photoluminescence of conjugated polymers remain to be elucidated, for example: (i) the broad and often structureless emission spectrum; (ii) the large apparent Stokes shift between the emission and absorption maxima; (iii) the rather small fluorescence quantum yield ($\phi_f \sim 10^{-5}$ to 10^{-1}); and (iv) the nonexponential photoluminescence decay dynamics. Recent studies of the role of supramolecular structure and morphology on *interchain* photoprocesses in conjugated polymers have led to the discovery of the central role of *intermolecular excimers* in the photophysics of the materials^[4-6]. Here, I will briefly discuss both of these excited-state complexes, excimers and exciplexes, of π -conjugated polymers.

2. Excimers and the Photophysics of Conjugated Polymers

Although *intermolecular excimers*^[12-14], first observed in aromatic molecules in 1954^[14], have been widely observed and studied in small molecules and in vinyl polymers bearing side-chain aromatic chromophores, they have not been explored in the photophysics of conjugated polymers in large part because of the apparent success of the quasi-one-dimensional description of the materials. Photoexcitations and excited states in conjugated polymers were described in terms of *intrachain* processes and *interchain* processes, if considered, were thought to be negligible. An essentially *interchain* model which describes part of the photoexcitation of PPV in terms of *polaron pairs*, i.e. negative and positive polarons on adjacent chains, was recently proposed^[10]. However, it should be pointed out that the proposed polaron pairs^[10] are neither identical nor equivalent to excimers.

Our recent studies of many conjugated rigid-rod polymers, such as poly(*p*-phenylene benzobisthiazole) (PBZT, 1), poly(*p*-phenylene benzobisoxazole) (PBO, 2), and poly(2,5-pyridyl-benzobisthiazole) (PPyBT, 3), in the form of thin films, solutions, and blends with nonconjugated polymers such as poly(methyl methacrylate) (PMMA), have shown conclusively that *intermolecular excimers* are formed efficiently in excited π -conjugated polymers^[4,11]. A simplified kinetic model of the intermolecular excited-state complex (excimer) formation is illustrated in scheme 1. In this scheme, originally proposed by Birks^[12], A* is an excited chromophore on a conjugated polymer chain, A is an unexcited chromophore on an adjacent chain, and (AA)* represents an excimer. The parameters k_{nr} and k'_{nr} are the sums of the rate constants for the nonradiative deactivation of the excited-state species, k_{rA} and k_{rAA} are the radiative rate constants for A* and (AA)* emission respectively, k_{-AA} is the excimer dissociation rate constant, k_E is the rate of excitation energy transfer to the excimer sites, and f_E is the fraction of "preformed excimer sites" in the conjugated polymer. Below the glass transition (T_g) of a conjugated polymer, only the fraction of the chromophores that are already aggregated in sandwich-type close packing ($\sim 3\text{-}4 \text{ \AA}$)^[15] will form excimers on excitation. In most π -conjugated polymers, except where prevented by design^[11], this requirement is usually met and the T_g is quite high so that the fraction of chromophores in preformed excimer sites, f_E , can be very high and may approach unity in some cases. Compared to the emission rate from an excited chromophore A*, the excitation transfer rate k_E is orders of magnitude faster. Thus, excimer formation is highly favored in π -conjugated polymers.

The luminescence of thin films of many conjugated polymers that we have investigated, such as 1-3, is primarily a result of excimer emission^[4]. However, blends of the conjugated polymers with PMMA or other nonconjugated polymers at low concentrations exhibit a highly structured emission identifiable as that of the isolated chromophore A* (Figure 1). The fluorescence quantum yield increased manyfold in going from thin films of the pure conjugated polymers to thin films of the

blends or of fluid solutions^[4]. This indicates that when the fraction of preformed excimer sites is zero ($f_E \sim 0$), as in dilute blends or fluid solutions, the quantum yield is increased as can be deduced from the excimer kinetic mechanism (scheme 1). The photoluminescence decay dynamics of the dilute blends or solutions of π -conjugated polymers also become describable by a single exponential kinetics^[4].

All the previously puzzling features of the photoluminescence of π -conjugated polymers, enumerated above, can be qualitatively explained by the excimer kinetic mechanism (scheme 1). The role of excimers is not limited to the photoluminescence of conjugated polymers but is expected as well in electroluminescence^[4,16]. Apart from luminescence, the excimer mechanism is also important in other photophysical processes in conjugated polymers, most notably charge photogeneration and photoconductivity^[6]. Thus, the future application of a range of photophysical techniques and theoretical modeling to the characterization of excimers in conjugated polymers will be essential to a full understanding of the photophysics of the materials and their development for various applications in optoelectronics.

3. Exciplexes of Conjugated Polymers

Ultrafast (< 1 ps) photoinduced electron transfer from electron donating PPV derivatives^[17a] and poly(3-alkylthiophenes)^[17b] to the strong electron acceptor C_{60} , resulting in complete charge separation, quenching of photoluminescence, and orders of magnitude enhancement of photoconductivity, was recently reported^[17]. Although by definition such fullerene/conjugated polymer composites are not strictly exciplexes^[13], they are clearly related and they also illustrate the rich scope of the excited-state photoprocesses in π -conjugated polymers. Our studies of several classes of heterocyclic conjugated rigid-rod polymers, such as 1-3, polybenzobisazoles, polyquinolines, and polyimines, have shown that they are weak electron acceptors (A) having IP and EA values and associated HOMO and LUMO energy levels that are tunable over a wide range. Binary mixtures of

these conjugated polymers with suitable donor molecules (D) such as tris(*p*-tolyl)amine (TTA) in the form of thin film bilayer assemblies or blends do not exhibit ground-state interactions. However, upon photoexcitation of such A/D assemblies or blends, *luminescent exciplexes* were formed as evidenced by a number of photophysical techniques, including transient (ps) absorption spectroscopy, steady state photoluminescence (PL), picosecond PL decay dynamics, and photoinduced charge generation^[4-6]. Some of the remarkable properties of exciplexes of conjugated polymers include manyfold enhancement of luminescence quantum yield^[4-5], orders of magnitude enhancement of quantum efficiency of photocarrier generation^[6], and the exciplex emission and the photophysical properties which are tunable by the IP and EA values of the exciplex components^[4-6]. The possible enhancement of nonlinear optical properties in conjugated polymer exciplexes owing to their dipole moments, and the new optical channels they imply, is also currently being explored. Exciplexes of conjugated polymers thus add to conducting polymers in expanding the theoretical and experimental scope of conjugated polymers.

4. Acknowledgment

This research was supported in part by the NSF (CTS-9311741), the Center for Photoinduced Charge Transfer and the Office of Naval Research. The contributions of John Osaheni, Anita Alanko, and Jason Haak are acknowledged and thanked.

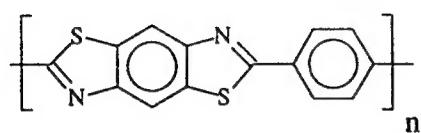
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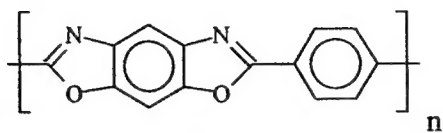
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Figure Captions

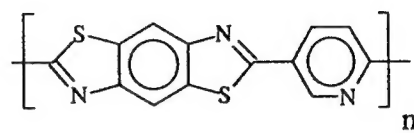
Figure 1: Photoluminescence spectra at room temperature: (a) thin film of PPyBT (3); (b) thin films of PPyBT/PMMA blends. The excitation wavelength was 400 and 440 nm for the PL spectra of (b) and (a) respectively.



1



2



3

Scheme 1

